Wetting of Polyethylene by Water, Methylene Iodide and Methylene Iodide–Decalin Mixtures

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The wettability of oxidized polyethylene films was studied with pure liquids (water and methylene iodide) and practically nonpolar mixtures of Decalin and methylene iodide. A linear variation was found of the wettability of these films with the chemical composition of their surfaces (determined by adsorption of radioactive ^{45}Ca ions).

A value of γ_s^d for the polyethylene was found with the nonpolar mixtures of methylene iodide and Decalin and the values of the solid–liquid polar interactions (I_{sl}^p) for oxidized polyethylene were deduced.

Dipole–dipole and induced dipole–dipole interactions between the pure liquids and the oxidized and unoxidized polyethylene were calculated for two possible orientations of the hydrocarbon chains to the surface and compared with the experimental results. Generally a poor agreement was obtained, mainly due to the difficulty in estimating the correct values for the distances between molecules or groups. However, a better agreement was obtained assuming that the chains were perpendicular to the surface.

INTRODUCTION

The relation between the wetting of a solid by liquids and its adsorption capacity has been studied by various authors. Rehbinder *et al.* (1) and Doss and Rao (2) have derived theoretical expressions for the wetting isotherms. Ruch and Bartell (3) set up a model of wetting for a hydrophilic surface by aqueous solutions of decylamine, combining the data of solute adsorption, contact angle measurements and adhesion tensions.

Tsunoda (4), Tsunoda, Seimiya, and Sasaki (5), and quite recently Seimiya, Saito, and Sasaki (6) established the wetting isotherm for a hydrophobic surface of paraffin in contact with fatty alcohol homologues and aqueous sodium stearate solutions. Adsorption and wetting studies on paraffin have been made by Guastalla (7) with saturated acid and alcohol solutions, and by Padday (8) who calculated the adhesive forces opera-

ting at the water–paraffin and tetradecyltrimethylammonium bromide solution–paraffin interfaces.

The relation between the free energy of adhesion and the free energy of molecular reactions of exchange at solid–liquid interface was interpreted by Ter-Minassian-Saraga (9) by statistical thermodynamical calculations.

Girafaleo and Good (10), Good and Hope (11), Good and Elbing (12), and Fowkes (13), using the theory of intermolecular forces involved in the solid–liquid and liquid–liquid interactions set up methods of deriving the free energy of adhesion for solids with liquids from the surface free energies of the adhering phases. These methods were recently used to study the adhesive forces of hydrophobic polymer surfaces in contact with polar and nonpolar liquids (14, 15). It should be noticed that the wettability studies of polymer surfaces have a considerable significance due to their

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application to the different practical processes (16–20).

In this paper we present results of experiments performed with mixtures of practically nonpolar methylene iodide and Decalin and with polar water in contact with unoxidized and oxidized low density polyethylene.

The infrared spectroscopy studies of oxidized polyethylene showed that carbonyl polar groups are found in a very thin superficial layer on the oxidized polyethylene (21–23).

Using this result and ours we set up a model of the process of wetting where the degree of chemical attack (oxidation) of the polyethylene is related to the chemical nature and composition of its surface as determined by the adsorption of calcium ions.

We have also attempted to calculate the energies of interaction between the polar groups at the solid–liquid interfaces of our system and to compare them with those obtained from experimental measurements.

EXPERIMENTAL METHODS

Materials

Polyethylene. The low density polyethylene ($0.9299/cm^3$ at 23°C) thin film (19 μm) used in this study was Cryovac L Film produced by "Grace Société" France. Circular samples were purified in carbon tetrachloride for 15 min and subsequently extracted with boiling acetone for 5 hr. This time of extraction led to reproducible values of the contact angle. After extraction the films were dried under reduced pressure at room temperature. Cleaned specimens were used for oxidation and wettability measurements.

Oxidizing mixtures were prepared from sulfuric acid (sp gr 1.84, pure grade) and potassium chlorate (reagent grade).

Water. Tridistilled from permanganate solution in all Pyrex apparatus.

Decalin. Technical grade Decalin was passed through the silica gel column and subsequently distilled three times under normal pressure. Fraction boiling at 185°C was collected. It

was assumed that the collected fraction was *trans*-Decalin.

Methylene iodide. AR Rhône Poulenc grade was used as received.

^{45}Ca calcium chloride was obtained from Commissariat à l'Energie Nucléaire, France. Its specific activity used for experiments was approximately 100 mCi/g.

Methods

Contact angles. The contact angles of chemically treated and untreated polyethylene were measured at room temperature by the drop-on-plate method by means of the apparatus described elsewhere (24). All reported values are the average of at least six measurements. The average experimental error of the measurement was about 2°. Advancing contact angles were used for all plots and calculations, as in the advancing stage the solid surface may be considered to be practically free of any adsorbed vapor.

Surface tension measurements. A Wilhelmy-type microelectrobalance produced by C. I. Electonics Ltd. was used to measure the surface tension of Decalin–methylene iodide mixtures.

Adsorption measurements. To determine the surface density of the polar sites C=O created by oxidation at the surface of polyethylene a radiotracer method reported elsewhere (25) was used. The polyethylene films 30 mm in diameter were placed on the surface of an aqueous solution of ^{45}Ca-labeled calcium chloride. The amount of Ca^{2+} ions adsorbed at a given polyethylene/solution interface was deduced from the radioactivity detected above the film by a thin window Geiger-Muller tube. The apparatus and the details of these experiments were reported elsewhere (24, 26).

Oxidation. Samples of purified polyethylene film were immersed in sulfuric acid–potassium chlorate mixtures of various compositions at a constant temperature (20°C). The duration of immersion has been varied. Then the samples were rinsed several times with distilled water, dried in a desiccator under reduced pressure,
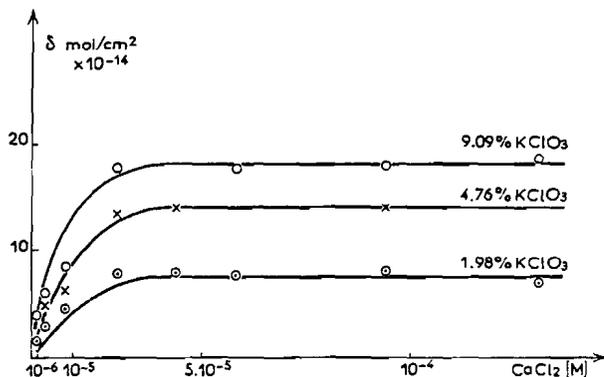
FIG. 1. Isotherms of adsorption of Ca^{2+} ions at the interface oxidized polyethylene/solution of $CaCl_2$. δ = surface density of Ca^{2+} ions vs $CaCl_2$ concentration in solution. Three oxidizing mixtures (wt%); 20°C; time of immersion 30 sec.

and used for contact angle and adsorption measurements.

It has been found that for times of immersion longer than 10 sec the contact angles had constant values.

RESULTS

Polyethylene–Water System

The isotherms of adsorption of the Ca^{2+} ions on the oxidized films are shown in Fig. 1. Saturation values were obtained for each

composition of oxidizing mixture. These isotherms are of the Langmuir type 1. The equilibrium constant is independent of the degree of oxidation of the surface and equal to $K = 1.65 \times 10^5$ liters/mole.

The amount δ of created polar sites at the polyethylene surface varies with the concentration of potassium chlorate in the oxidizing mixture. This effect is shown in Fig. 2.

The contact angles have been measured for each degree of oxidation of polyethylene. Their values are listed in Table I.
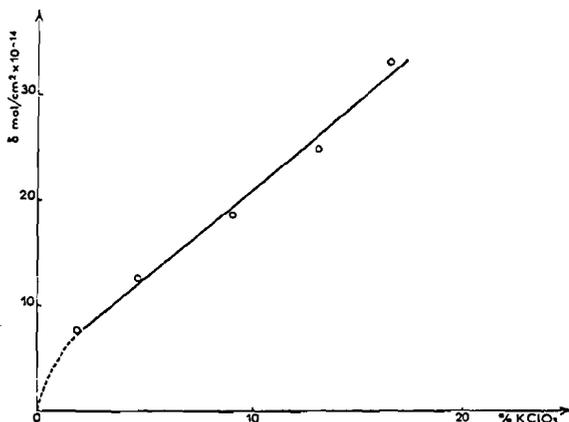

FIG. 2. Surface density of the polar groups vs potassium chlorate concentration (% of wt) in the oxidizing mixture; 20°C; 30 sec.

TABLE I

CONTACT ANGLES, WORKS OF ADHESION AND I_{sl}^p FOR POLYETHYLENE-WATER SYSTEM[a]

θ	Concn. of KClO$_3$ in the oxidizing mixtures (%)					
	0.37	1.98	4.76	9.09	13.03	16.6
θ	96	94	88	80	74	70	68
W_A	64.98	67.15	74.72	84.47	92.42	96.75	98.9
I_{sl}^p	11.54	13.71	20.88	31.03	38.98	43.31	45.5

[a] When: $\gamma_l = 72.2$ dyn/cm; $\gamma_l^d = 21.8$ dyn/cm; $\gamma_s^d = 32.75$ dyn/cm.

Polyethylene–Methylene Iodide/Decalin Mixtures System

The surface tension of methylene iodide–Decalin mixtures is plotted vs the concentration of methylene iodide in Fig. 3, and listed in Table II. Strong adsorption of Decalin molecules at the air-mixture interface may be inferred from the rapid fall of the surface tension of the mixture at concentrations of Decalin between 5–20%.

Table III lists the contact angles and the corresponding works of adhesion of the mixtures with unoxidized and oxidized polyethylene.

The works of adhesion of the mixtures with polyethylene are plotted vs the amount of polar sites on its surface in Fig. 4.

For the different mixtures an average slope equal to 0.19×10^{-14} erg/mole of site was obtained.

Zisman's type curves (27) are presented in Fig. 5 for methylene iodide mixtures in contact with oxidized and unoxidized polyethylene. We note that the critical surface tension γ_c for unoxidized polyethylene is equal to 32.75
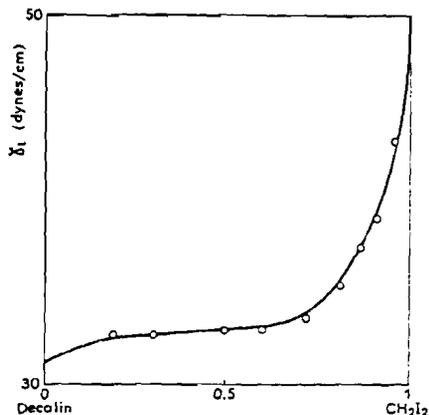

FIG. 3. Surface tension γ_l of Decalin–methylene iodide mixtures vs methylene iodide concentration in the mixture (volume fraction).

dyn/cm. It increases with the degree of oxidation of polyethylene.

We represent in Fig. 6 the variation of the work of adhesion of pure water and methylene iodide as a function of the density of polar sites at the surface of the polyethylene. The flat linear segment of curve 1 indicates that the work of adhesion of the oxidized polyethylene with water approaches a limiting value. The slopes for methylene iodide or water on polyethylene are, respectively, equal to 0.26 $\times 10^{-14}$ and 1.4×10^{-14} erg/mole of sites.

Work of Adhesion: Nonpolar and Polar Contributions

The free energy of interaction W_A between two phases across a plane boundary originates from London dispersion forces W_A^d and from

TABLE II

SURFACE TENSIONS OF METHYLENE IODIDE–DECALIN MIXTURES AND THEIR DISPERSION ENERGIES WITH NONTREATED POLYETHYLENE[a]

	Vol ratio methylene iodide–Decalin						
	100:0	95:5	90:10	85:15	80:20	70:30	60:40
γ	50.4	43.07	40.0	37.1	35.2	33.7	33.2
γ^d	50.4	43.07	40.0	37.1	35.2	33.7	33.2
$W_A^d = 2(\gamma^d \gamma_s^d)^{\frac{1}{2}}$	81.26	75.12	72.40	69.63	67.81	65.95	65.91

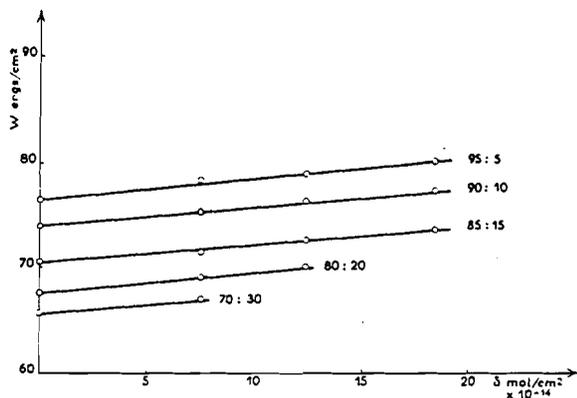[a] When $\gamma_s^d = 32.75$ dyn/cm.

FIG. 4. Works of adhesion W vs density δ of polar groups of the oxidized polyethylene for different concentrations (vol %) of methylene iodide in the methylene iodide/Decalin mixtures.

the polar forces. The latter are mainly due to the dipole–dipole and dipole–induced dipole interactions.

TABLE III

CONTACT ANGLES, WORKS OF ADHESION AND $I_{sl}{}^p$ FOR METHYLENE IODIDE–DECALIN MIX- TURES ON POLYETHYLENE[a]

MeI/D vol ratio		Concn. of KClO$_3$ in the oxidizing mixture (%)				
		0	0.37	1.98	4.76	9.09
100:0	θ	47	46	44	42	39
	W_A	84.77	85.43	86.64	87.85	89.56
	$I_{sl}{}^p$	3.51	4.17	5.38	6.59	8.30
95:5	θ	39	37	35	34	31
	W_A	76.54	77.44	78.34	78.78	80.0
	$I_{sl}{}^p$	1.42	2.32	3.22	3.66	4.88
90:10	θ	33	31	28	25	21
	W_A	73.92	74.29	75.32	76.24	77.32
	$I_{sl}{}^p$	1.52	1.89	2.92	3.84	4.92
85:15	θ	27	25	22	17	11
	W_A	70.45	70.71	71.49	72.57	73.53
	$I_{sl}{}^p$	0.53	1.08	1.86	2.94	3.90
80:20	θ	22	19	15	6	0
	W_A	67.82	68.50	69.20	70.22	70.4
	$I_{sl}{}^p$	0.02	0.69	1.39	2.41	2.51
70:30	θ	17	13	7	0	0
	W_A	65.92	66.52	67.16	67.4	67.4
	$I_{sl}{}^p$	0.03	0.57	1.21	1.45	1.45

[a] When $\gamma_s{}^d = 32.75$ dyn/cm.

If the system consists of a polar solid and a polar liquid the dispersion forces contribution may be separated from the polar forces contribution. $W_A{}^d$ is defined by the relation $W_A{}^d = 2(\gamma_l{}^d\gamma_s{}^d)^{\frac{1}{2}}$ (13). The main difficulty in the evaluation of $W_A{}^d$ is the knowledge of a correct value for $\gamma_s{}^d$. It was shown (10, 27) that the critical surface tension γ_c approaches $\gamma_s{}^d$ if γ_c is deduced from measurements of the contact angles with nonpolar liquids. However, for polyethylene, having a value of γ_c above 30 dyn/cm, such a series of pure liquids does not exist.

Fowkes (28) has shown that the surface tension of methylene iodide may be accounted for almost entirely by its dispersion force component ($\gamma_l{}^d = 48.5 \pm 9$ dyn/cm), although this substance possesses a relatively high dipole moment value (Table IV).

It was assumed, then, that the employed mixtures, having surface tensions close to the value γ_c, may be fully accounted for by their dispersion force components (Table II).

Substracting the values of the dispersion energy of adhesion $W_A{}^d$ from the total adhesion energy $W_A = \gamma_l(1 + \cos\theta) + \pi_s$ and neglecting the unknown term π_s which is the reduction in surface energy of the solid resulting from adsorption of vapor from the liquid—the polar interaction term
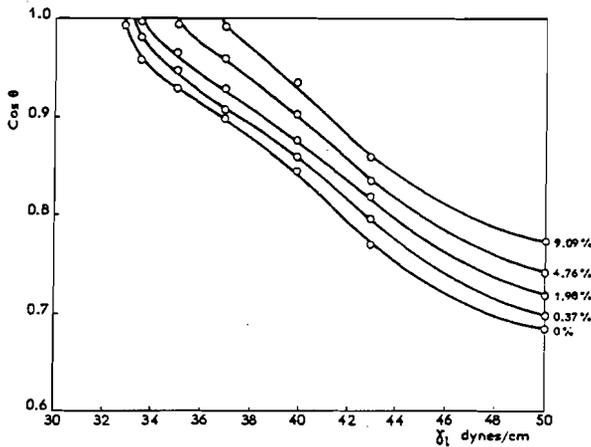
$$I_{sl}{}^p = (\cos\theta + 1)_{\gamma_l} - 2(\gamma_l{}^d\gamma_s{}^d)^{\frac{1}{2}}$$

FIG. 5. Contact angles ($\cos\theta$) vs surfce tension γ_l of methylene iodide/Decalin mixtures on polyethylene with different degrees of oxidation at constant potassium chlorate concentration in the oxidizing mixture.

(14) corresponding to the different degrees of polyethylene oxidation was obtained. The neglect of the term π_s may give I_{sl}^p values lower than the real ones. The nonpolar ($W_A{}^d$) and polar (I_{sl}^p) contributions to the total energy of adhesion of water and methylene iodide mixtures to polyethylene are summarized in Tables I, II, III.

The polar contributions to the energy of adhesion for the surface of oxidized polyethylene are much higher with a polar liquid like water than with the slightly polar methylene iodide.

INTERPRETATION

Model of Wetting of Real Solid by a Pure Liquid

The model of unoxidized and oxidized polyethylene surfaces is shown in Fig. 7. The random distribution of the molecules of the liquid and of CH_2 and $C=O$ groups at the liquid–solid interface is assumed. At saturation of oxidation the surface comprises only $C=O$ groups.

Let $N = \delta_{max}$ represent the number of CH_2 groups per square centimeter, δ—the surface density of $C=O$ groups (as measured by ^{45}Ca

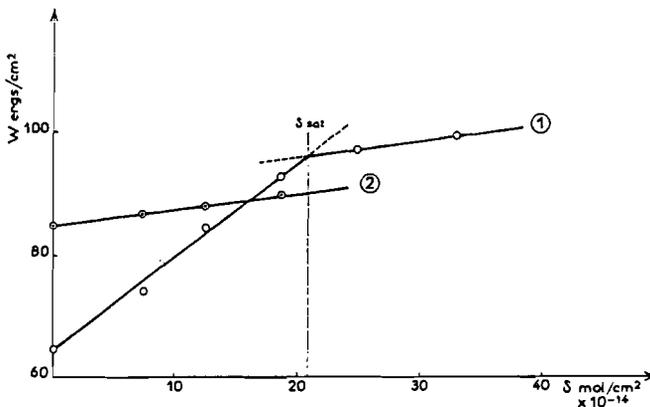FIG. 6. Works of adhesion W vs density δ of polar groups in the oxidized polyethylene:water (1) and methylene iodide (2).
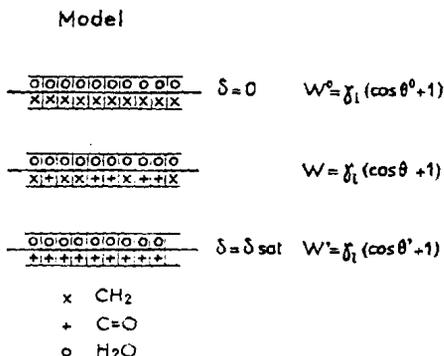
Model

FIG. 7. Model of wetting by pure liquid of unoxidized and oxidized polyethylene. W^0 and $\cos\theta^0$—values for unoxidized polyethylene; W'' and $\cos\theta'$—values for oxidized polyethylene.

adsorption) and ω = the average area per CH_2 group at the surface of polyethylene. Then, the fraction of the surface occupied by the $C=O$ groups may be represented by the ratio

$$x = \frac{\delta}{\delta_{max}} = \delta \cdot \omega \quad 0 \leqslant x \leqslant 1. \quad [1]$$

The energies of adhesion of a pure liquid to the surfaces of polyethylene of different degrees of oxidation are, respectively,

$$W^0 = \gamma_l(\cos\theta^0 + 1) \quad \text{for} \quad x = 0 \quad [2]$$

$$W = \gamma_l(\cos\theta + 1) \quad \text{for} \quad 0 \leqslant x \leqslant 1 \quad [3]$$

$$W' = \gamma_l(\cos\theta' + 1) \quad \text{for} \quad x = 1, \quad [4]$$

where W^0 and θ^0 are the work of adhesion and the contact angle of the liquid on unoxidized polyethylene; W' and θ' the work of adhesion

TABLE IV

DIPOLE MOMENTS, INTERMOLECULAR DISTANCES AND POLARIZABILITIES OF THE MOLECULES OR GROUPS STUDIED

Molecule or group	μ ($\times 10^{-18}$ esu-erg)	d ($\times 10^{-8}$ cm)	α ($\times 10^{-24}$ cm³/mole)
H_2O	1.87 (30)	1.55	1.49 (31)
CH_2I_2	1.1 (30)	2.8	12.83 (32)
$C=O$	2.7	2.0	
C_{A2}		2.26	2.02 (13)

and the contact angle of the liquid on fully oxidized polyethylene.

For a given oxidized surface, the work of adhesion (Eq. [3]) may also be represented as follows:

$$W + W^0(1 - x) + W'x. \quad [5]$$

This leads to the final equations for the work of adhesion and $\cos\theta$ on a given oxidized surface

$$W = W^0 + \frac{\delta}{\delta_{max}}(W' - W^0), \quad [6]$$

and

$$\cos\theta = \cos\theta^0 + \frac{\delta}{\delta_{max}}(\cos\theta' - \cos\theta^0). \quad [7]$$

However the relations [6] and [7] are not complete. The experimental terms of W and W' are measured on the real surface of the polyethylene, whereas the last term of these is related to the apparent surface Ω_{app} equal to 1 cm². Thus the last term of these equations should be allowed for a roughness factor $\varphi = \Omega_r/\Omega_{app}$ where Ω_r is the real area. We obtain instead of [6] and [7] the relations

$$W = W^0 + \frac{\delta\omega}{\varphi}(W' - W^0), \quad [8]$$

and

$$\cos\theta = \cos\theta^0 + \frac{\delta\omega}{\varphi}(\cos\theta' - \cos\theta^0). \quad [9]$$

The roughness factor φ may be deduced from the break point of the Fig. 6 (curve 1). Above this point the work of adhesion and the contact angle reaches a saturation value; further oxidation creates groups below the interface of polyethylene. As $\delta_{sat} = \Omega_r\delta_{max}$, we write

$$\varphi = \frac{\delta_{sat}}{\delta_{max}}. \quad [10]$$

Assuming that the hydrocarbon chains are parallel to the surface of polyethylene, the average area ω per CH_2 (or $C=O$) group is according to Ref. (13) equal to 5.9 Å².

With the experimental value $\delta_{sat} = 21.0 \times 10^{14}$ sites/cm² found on Fig. 6 and with δ_{max}
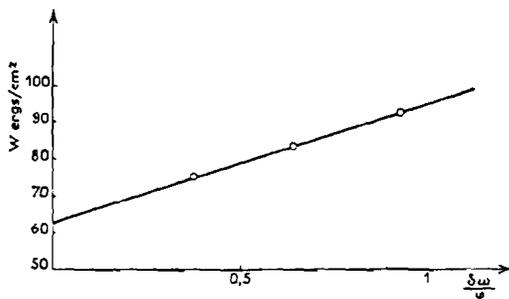
FIG. 8. Work of adhesion W of water with oxidized polyethylene vs relative concentration of the polar groups at the real solid-liquid interface calculated according to Eq. [8].

$= 1/\omega = 16.8 \times 10^{14}$ sites/cm², we obtain $\varphi = 1.25$.

However if we assume that the hydrocarbon chains are normal to the surface of polyethylene, then according to Ref. (13), the average area per CH₃ group is 20 Å² and $\delta_{max} = 1/\omega = 5.0 \times 10^{14}$ sites/cm². The roughness factor in this case is $\varphi = 4.2$.

When the work of adhesion W of water with oxidized polyethylene is plotted vs $\delta\omega/\varphi$ (Fig. 8) the same linear relation for both values of φ is found because ω/φ is independent of orientation of hydrocarbon chains to the surface of polyethylene.

The slope of the straight line is equal to $W'' - W'^0$ and the intercept is W'^0. The work of adhesion W'' corresponding to the polyethylene surface saturated with C=O groups is 94.1 dyn/cm and we deduced $\theta' = 72°21'$.

The calculated value of the work of adhesion W'^0 of unoxidized polyethylene with water is equal to 63 dyn/cm. This value is in a good agreement with the experimental value 64.9 dyn/cm.

Calculation of Polar Forces

The energy of dipole–induced dipole interaction for a pair of molecules or groups of atoms is defined by (29)

$$\epsilon_{did} = \frac{2\alpha\mu^2}{a^6}, \qquad [11]$$

where α is the polarizability of the nonpolar

unit; μ the dipole moment of the polar one; and a the distance between the centers of the two groups or units. Equation [11] applies to the case of unoxidized polyethylene in contact with polar water and methyl iodide. When it is oxidized the surface of polyethylene consists of CH₂ and C=O groups. The latter are dipoles and their interactions with water and methylene iodide groups are the interactions of two permanent dipoles, one of which (C=O) is supposed to have a given orientation.

The maximum energy of interaction between two permanent dipoles is given by the following equation (29):

$$\epsilon_{dd} = \frac{2\mu_1\mu_2}{a^3}, \qquad [12]$$

where μ_1 and μ_2 are the dipole moments of the interacting molecules or groups of atoms and, a, is the distance between their centers.

Table IV lists the values used to calculate the polar interactions of dipole–dipole type and dipole–induced dipole type.
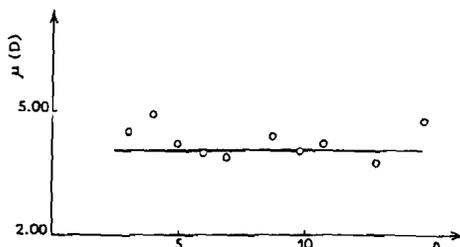

FIG. 9. Dipole moments of aliphatic ketones vs the number of carbons in the alkyl radical.

TABLE V

ATOMIC AND EXTERIOR (VAN DER WAALS) RADII

	r_a ($\times 10^{-8}$ cm)	r_w ($\times 10^{-8}$ cm)
H	0.29	1.20
C	0.77	
O	0.66	1.40
I	1.33	2.15

The dipole moment value for C=O group was taken as an average value of the dipole moments of liquid aliphatic ketones. Figure 9 represents the dipole moments of these ketones as a function of the alkyl chain length.

To calculate the distances d between the centers of the dipoles and the outer boundary of the molecule adsorbed on interfacial plane, the models of these molecules and groups, conforming to their spacial configuration, using the values of the atomic and exterior (Van der Waals) radii, were set up. Table V contains the values of these radii for different atoms which form the studied molecules and the groups of atoms. All values were taken from Ref. (29).

In Figs. 10 and 11 models of the water, methylene iodide molecules and CH_2, C=O groups are shown. It was assumed that the center, 0, of the dipole is located halfway between the centers of the atoms.

The further assumption made was that the methylene iodide molecule is oriented with its hydrogen atom towards the C=O group (Fig. 10a) and that the water molecule may face the

TABLE VI

DISTANCES BETWEEN THE CENTERS OF INTERACTING MOLECULES OR GROUPS, THEIR DIPOLE-INDUCED DIPOLE AND DIPOLE-DIPOLE ENERGIES

Pair of contacts	a ($\times 10^{-8}$ cm)	ϵ_{dd} ($\times 10^{-14}$ erg/site)	ϵ_{did} ($\times 10^{-14}$ erg/site)
CH_2-H_2O	3.81		0.46
$CH_2-CH_2I_2$	5.06		0.029
$H_2O-C=O$	3.55	22.57	1.09
$CH_2I_2-C=O$	4.80	5.37	1.51

interface with two possible orientations (an average of d_I and d_{II} was considered; see Fig. 10b).

The distances a_1, a_2, a_3, a_4 between the centers 0 of the interacting dipoles or dipoles and groups (as for the induced dipoles calculations) are the sum of corresponding d values.

Table VI shows the values of intermolecular distances for the studied systems and the calculated energies for each pair of contacts. As shown, the induction energies on the unoxidized polyethylene are very small and negligible compared to the dipole–dipole interactions.

The calculated energies of dipole–dipole interactions were compared with the experimental values. The ratio of the two slopes of the lines of Fig. 6 may be expressed as a function of the interaction energies ϵ_{did} and ϵ_{dd} between water and polyethylene and methylene iodide and polyethylene. It is justified to write the following relation:

$$\frac{(W' - W^0)H_2O}{(W' - W^0)CH_2I_2} = \frac{\dfrac{2\mu_{H_2O}\mu_{C=O}}{a_1^3} + \dfrac{2\alpha_{H_2O}(\mu_{C=O})^2}{a_1^6} - \dfrac{2\alpha_{CH_2}(\mu_{H_2O})^2}{a_3^6}}{\dfrac{2\mu_{CH_2I_2}\mu_{C=O}}{a_2^3} + \dfrac{2\alpha_{CH_2I_2}(\mu_{C=O})^2}{a_2^6} - \dfrac{2\alpha_{CH_2}(\mu_{CH_2I_2})^2}{a_4^6}}$$ [13]

The experimental ratio of the slopes from Fig. 6 gives the value of 5.62, the corresponding calculated value is 3.39.

It should be noticed, that an error of 0.3 Å in the estimation of intermolecular distances a

between the centers of the dipoles brings along a considerable discrepancy (30%) between the calculated and experimental values of the ratio.

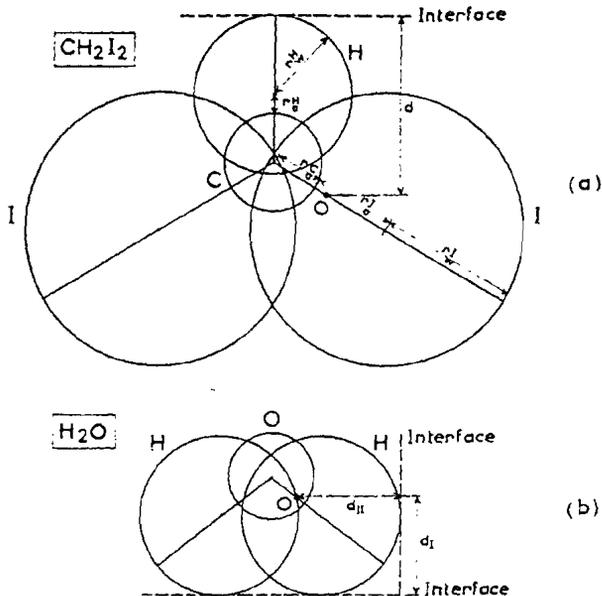If the calculated values ϵ_{dd} obtained for a pair of interacting dipoles were multiplied by

Fig. 10. Distances for polyethylene and methylene iodide or water.

δ_{max}, φ, the energy for 1 cm^2 was found. This energy for water-oxidized polyethylene (assuming the parallel configuration of the hydrocarbon chains to the surface of polyethylene) is: $(22.57 \times 10^{-14}$ erg/site $\times 16.8 \times 10^{14}$ sites/cm$^2)/1.25 = 303.3$ erg/cm^2 and for methylene iodide-oxidized polyethylene equal to: $(5.37 \times 10^{-14}$ erg/site $\times 16.8 \times 10^{14}$ sites/cm$^2)/1.25 = 72.16$ erg/cm^2.

It should be noted, however, that the above calculations are not completely justified as the number of the sites was overestimated. The maximum number should be obtained by counting every other CH$_2$. If every CH$_2$ were oxidized to C=O, the chain would be chemically unstable. Therefore, the area per 2CH$_2$ is either about 12.4 or 11.2 Å^2, depending on crystal plane, as calculated from the crystal structure (36). If the surface is not perfectly crystalline, the area per polar site will be much larger. Consequently a higher value of ω, a lower δ_{max} and an increase of the roughness factor φ will be obtained. These parameters will lead to lower calculated contributions to the
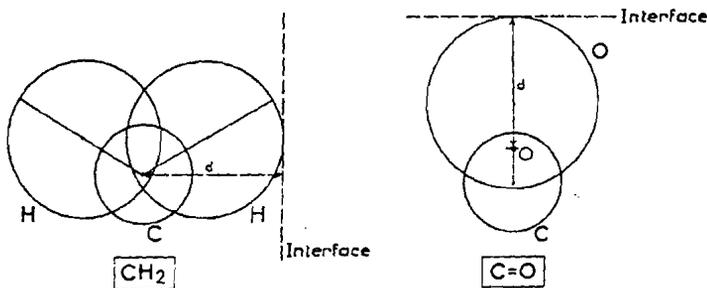

Fig. 11. Distances between the groups CH$_2$ and C=O of polyethylene and the molecules of the wetting liquids.

electrostatic energies of interactions between oxidized polyethylene and water or methylene iodide.

Lastly, considering the normal configuration of hydrocarbon chains to the surface of polyethylene we obtain the following results: for water-oxidized polyethylene $(22.57 \times 10^{-14}$ erg/site $\times 5.0 \times 10^{14}$ site/cm$^2)/4.2 = 26.9$ erg/cm^2 and for methylene iodide-oxidized polyethylene $(5.37 \times 10^{-14}$ erg/site $\times 5.0 \times 10^{14}$ site/cm$^2)/4.2 = 6.4$ erg/cm^2. The Van der Waals radii of CH_3 and of CH_2 groups for the configuration shown in Fig. 11 are equal.

These results are in a good agreement with the experimental values of the polar contributions to the free energy of adhesion, which for water-oxidized polyethylene is 27.4 erg/cm^2 and for methylene iodide-oxidized polyethylene is 4.8 erg/cm^2.

The polar contribution to the work of adhesion of water and methylene iodide with unoxidized polyethylene is originating in the ϵ_{did} dipole–induced dipole interactions, and for 1 cm^2 equals $I_{s1}{}^p$ shown in Tables I and III.

To calculate these contributions the values for one contact ϵ_{did} (Table VI) are multiplied by δ_{max}. The introduction of the roughness factor seems to be not justified in this case. As it was shown (37) in the recent electron microscopy study of polypropylenes treated with chromic acid–phosphoric acid solutions the porous structure of the initially uniform polymer films was obtained during the treatment. The etching of the films, as shown on these micrographs, is relatively high. Similarly, the micrographs of our unoxidized polyethylene showed that its surface was apparently smooth (38).

For a parallel configuration of the hydrocarbon chains to the surface we obtain: unoxidized polyethylene–water, 0.46×10^{-14} erg/site $\times 16.8 \times 10^{14}$ site/cm$^2 = 7.72$ erg/cm^2; unoxidized polyethylene–CH_2I_2, 0.029×10^{-14} erg/site $\times 16.8 \times 10^{14}$ site/cm$^2 = 0.49$ erg/site. For a normal configuration of the chains we have: unoxidized polyethylene–water, 0.46×10^{-14} erg/site $\times 5.0 \times 10^{14}$ site/cm$^2 = 2.30$ erg/cm^2; unoxidized polyethylene–

CH_2I_2, 0.029×10^{-14} erg/site $\times 5.0 \times 10^{14}$ site/cm$^2 = 0.15$ erg/cm^2.

In the both cases the agreement with experimental values of $I_{s1}{}^p$ is not satisfactory.[1] The $I_{s1}{}^p$ values for water and methylene iodide with unoxidized polyethylene are, respectively, equal to 11.54 and 3.51 erg/cm^2. It should, however, be noted that we consider our untreated polyethylene as if it did not contain any polar groups. This assumption was initially made in our work, as we did not detect any calcium ions adsorbed at the surface of unoxidized polyethylene. The accuracy of the measurements especially from the dilute CaCl$_2$ solutions may not be sufficient to reveal 0.6×10^{13} C=O sites/cm^2. This value (3% of the saturation one) would eliminate the discrepancy between the calculated and the experimental values for dipole–induced dipole interactions on unoxidized polyethylene.

DISCUSSION AND CONCLUSION

The superficial oxidation of polyethylene is not changing the nature of molecules in the bulk of the solid. Thus the cohesive forces in the oxidized and unoxidized polyethylene are practically equal. We have, therefore, a particular system of a nonpolar solid in the bulk and polar at the surface.

Consequently the intermolecular forces operating at the interface between the oxidized polyethylene and water or Decalin methylene iodide mixture are both dispersion and polar forces, and we conclude that γ_c could not be equaled to $\gamma_s{}^d$. It follows that the wettability studies by the contact angle technique of such a system involve some difficulties in the estimation of $\gamma_s{}^d$ value. We feel, nevertheless, that the γ_c value found with these mixtures and unoxidized polyethylene ($\gamma_c = 32.75$ dyn/cm) may be the $\gamma_s{}^d$ value of the polymer.

[1] If the equation proposed by Van der Avoird and Hofelich (35) for the "induction" energy based on a quantum mechanical treatment and equal to $u_{i} = \alpha_1 \mu_2{}^2/2a^6$ is applied, the corresponding values for the different types of contacts are four times lower.

This value $\gamma_s{}^d = 32.75$ dyn/cm is higher than that reported by Zisman (27) with polar liquids ($\gamma_c = 31$ dyn/cm) and lower than the one Petke and Ray (33) found by their study of the temperature dependence of the contact angles on different polymers ($\gamma_c = 36.0$ dyn/cm). It is in a good agreement with the calculated value presented by Wu (34) based on the application of a modified Hildebrand-Scott equation for the estimation of critical surface tensions of nonpolar polymers ($\gamma_c = 32$ dyn/cm).

The increase of γ_c with the degree of oxidation may be due to the rise of the $\gamma_s{}^p$ contribution to the total γ_s, while the $\gamma_s{}^d$ contribution remains constant.

The polar contribution $I_{s1}{}^p$ to the adhesion of the Decalin–methylene iodide mixtures on unoxidized polyethylene increases with the concentration of the second component of these solutions (see Table III). This variation of $I_{s1}{}^p$ with the composition of the mixture may be due to an increasing concentration of methylene iodide molecules in the adsorbed layer at the solid–vapor interface. Decalin is not changing the chemical nature of the interface, but the adsorbed polar methylene iodide molecules add polar groups to the interface and bring about there the establishment of dipole–dipole contact. This fact is analogous to the increase of adhesion implied by the oxidation of polyethylene.

To interpret the linear variation of the work of adhesion W_A with the surface density of polar sites δ of the oxidized polyethylene, we have used an ideal model of wetting based on the additivity of molecular energies for each couple of contact at the interface. These energies were calculated according to molecular models and atomic distances in the gaseous state. However, the distances between the chemical groups in the solid and the molecules of the liquid in contact may be larger and may lead to considerable decrease of the calculated values of these energies.

It should also be noticed that the dipole–dipole and dipole–induced dipole interaction energies were evaluated assuming the dielectric constant to be equal to 1 (which corresponds to the vacuum medium).

The underestimation of these two factors may lead to the errors in the calculation of dipole–dipole interaction energies. They may partly explain the fact that the calculated energies for 1 cm² do not agree very well with the experimental values.

Moreover the absolute value of dipole–dipole interaction energy to the free energy of adhesion depends on the value of δ_{max} appearing in [8]. This factor is eliminated when the ratio of the slope of the lines in Fig. 6 is deduced according to Eq. [13]. This procedure avoids the error introduced by the geometry of the model of the interface in the evaluation of the energy of adhesion and enhances the effect of the polarity of the wetting liquid.

We assumed that at saturation every CH_2 group is changed by oxidation into a $C{=}O$ group which interacts with one molecule of liquid. If only a constant fraction of the $C{=}O$ groups detected by the ions ^{45}Ca were located in the first layer of the solid, the energy of adhesion would be the same fraction of the calculated value. In particular the chains may be parallel or normal to the surface of polyethylene and every second CH_2 could be oxidized.

It is worthwhile to add that if the Keesom equation for the average interaction energy between the two permanent dipoles (thus taking into account the possible orientation of molecules in all directions) $\epsilon_{dd} = \frac{2}{3}(\mu_1{}^2\mu_2{}^2/KTa^6)$ were applied, the same value would be found as with the equation used by us.

The intercept of the lines obtained by plotting W_A vs δ for the systems unoxidized polyethylene–water and unoxidized polyethylene–methylene iodide may be considered as originating in the induced dipole–dipole interactions. A satisfactory agreement was obtained when water wets the solid. But the calculated value obtained for methylene iodide is much smaller than the experimental one. The difference between these two liquids, when

unoxidized polyethylene is considered, may be due to the fact that water molecules adsorb on the hydrophobic polyethylene less than methylene iodide or that an undetectable amount of C=O groups are found at the surface of the unoxidized polyethylene.

In conclusion, the chemical attack of a solid may change its nature in a superficial region. But the modification of its wetting properties depends on the composition of the outermost layer of the solid.

Although the analytical method is unable to distinguish between this layer and those below, it gives information, however, on the modification of the composition of the outermost layer of the solid.

For a given modification the free energies of adhesion of one solid having a polar surface with different polar liquids is a function of the dipole moment of the molecules of the liquids and can be calculated using classical theories.

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